Basics of Glass and Glass-Ceramic Formulation

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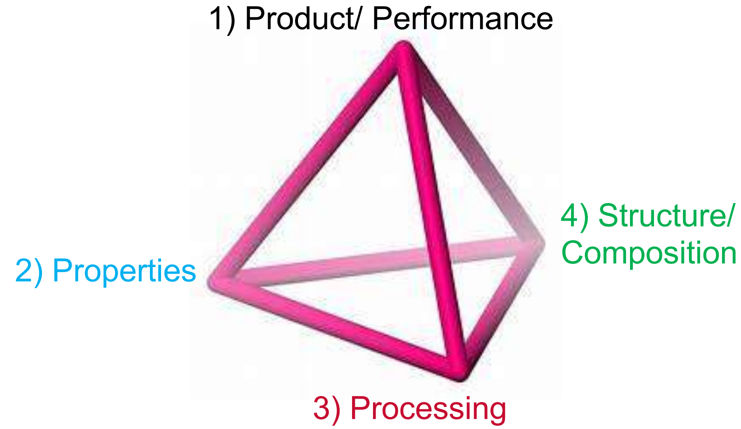
ICG Glass for a Sustainable Future
April 29-May 3, 2024
Lloret del Mar, Spain
29 April, 15:50-16:30

Considerations for Industrialization



1) **Product** considerations

- Commodity, high volume
- Specialty, low volume
- Can influence ability to change price, composition, processing

2) Final **properties**

- Application
- Life cycle:
  - Beer bottles vs phone cases vs nuclear waste storage
  - Product cycle (shipping, etc.)
  - Recyclability

3) **Processing**

- Interaction with equipment
- Redox
- Melting technology
- Batch/continuous
- Fuel

4) **Composition**/ Raw materials choices

- Purity, reproducibility
- Melt rate
- Availability
- Cost (margin)

€ $

Strategies for formulation

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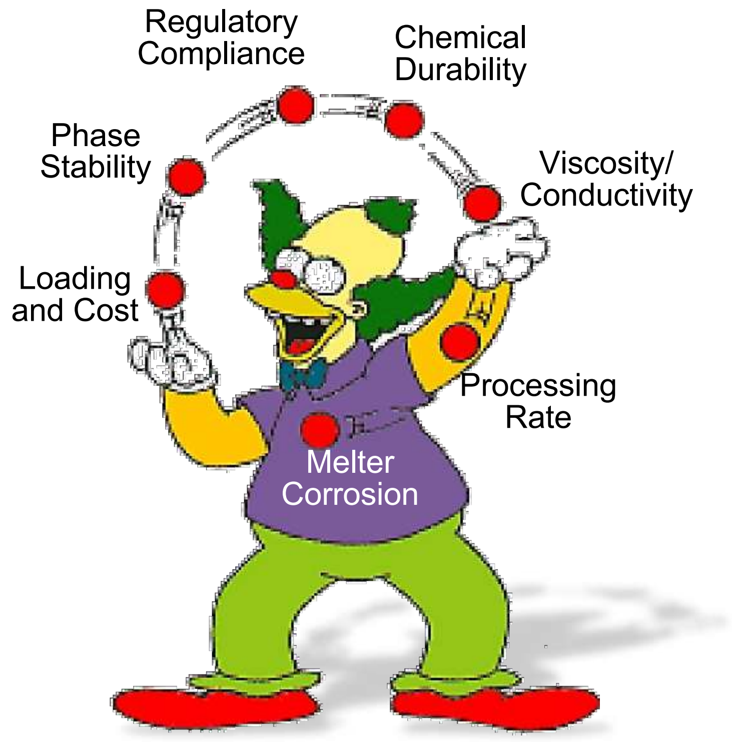
- Depends on the **goal**
  - Scientific understanding
    - i.e., with spectroscopy, structural investigation
  - Industrial processes optimization
    - Often unanalyzable complexities

- Goals in formulation
  - Property optimization
  - Processing constraints
  - Some factors may be more important



Juggling factors in nuclear waste glass formulation

Vienna 2014, SumGlass 2013 Proceedings, *Proc. Matl. Sci.* **7**:148-155

Simple strategies:
For understanding component effects

- **Experimental approaches**
  - One-at-a-time composition variation (add or substitute)
  - Change ratios
  - Leave-one-out
  - Compare substitution of one component at same level
- **Practical considerations**
  - Same composition different precursors
- **Structural model or metric**
  - Vary on other quantifiable metric affected by composition
- **Multi-component approaches**
  - Statistical design for empirical models
  - Machine learning

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FORMULATION STRATEGIES for

- Glasses
- Glass-ceramics

Primary examples from:

- Nuclear glass
- Optical glass

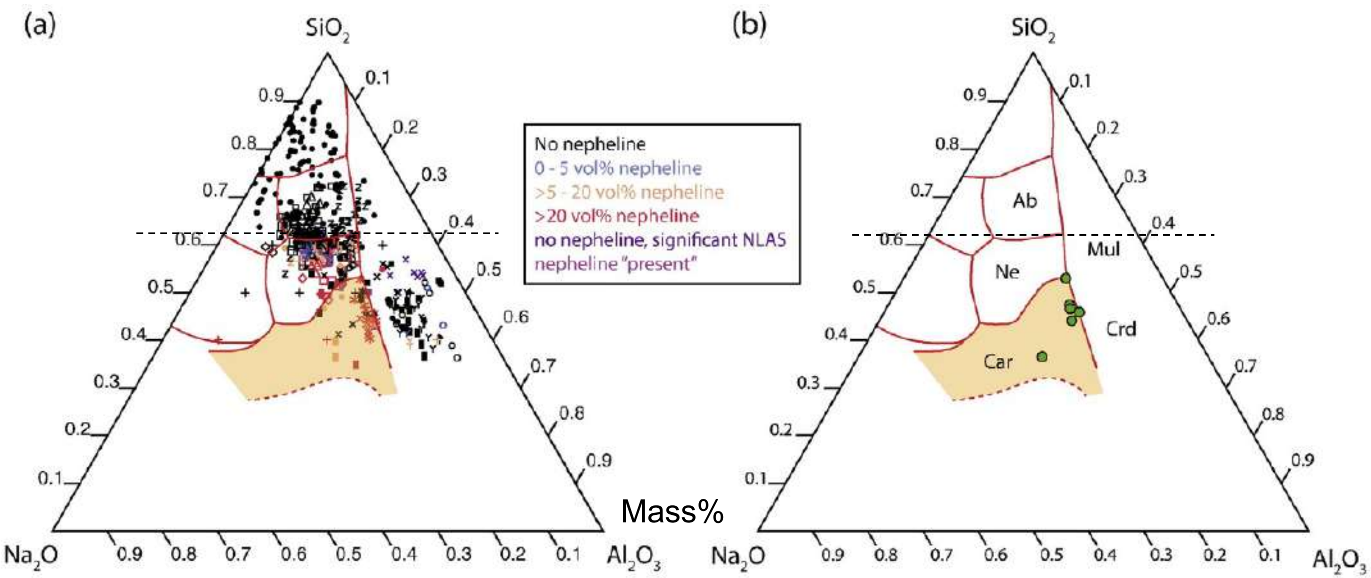
Glass families:

- Oxide
- Chalcogenide
- Fluoride
- Metallic

ICG TCs :
03 – structure and properties
05 – nuclear and hazardous waste vitrification
07 – nucleation, crystallization, & glass ceramics
18 – glass melting technology

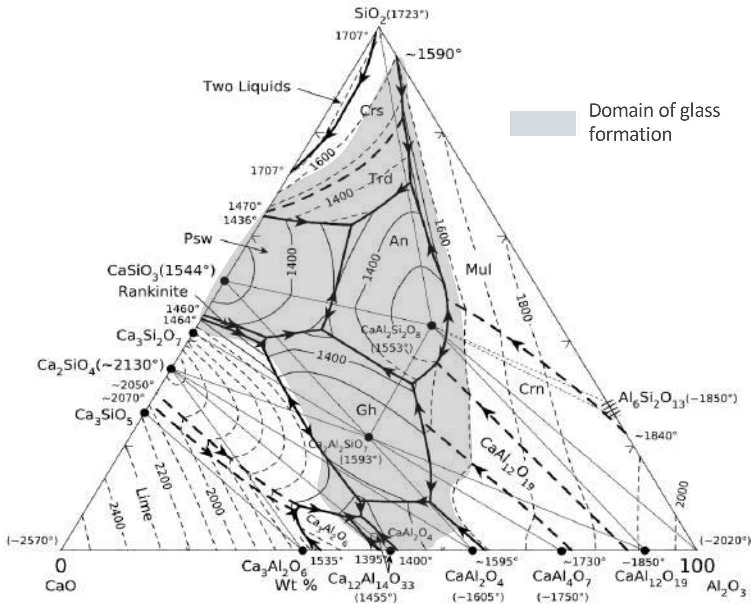
Phase diagrams
Glass-forming & crystallization

- **Na_2O-Al_2O_3-SiO_2**
  - Nepheline crystallization
  - Limits on [SiO_2] based on phase diagram ("nepheline discriminator")



Li, Hrma, Vienna, et al, *JNCS* 331, 202 (2003) McCloy et al, *JNCS* 409, 149 (2015)

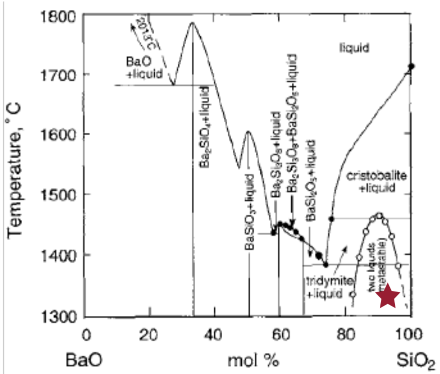
- **CaO-Al_2O_3-SiO_2**
  - PIVIC glass phase
  - (procédé d'incinération-vitrification in can)



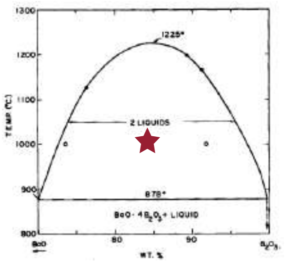
Perret et al – DEM 2021

Phase diagrams
Phase separation

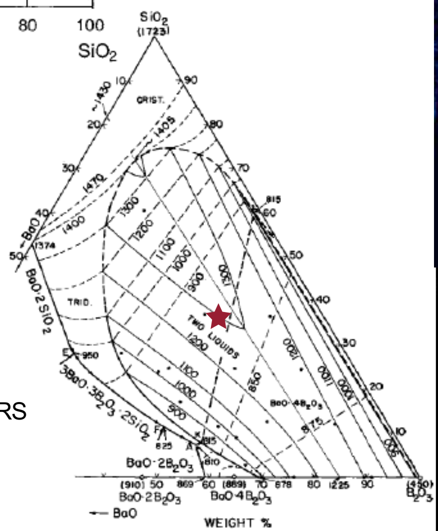
$BaO-B_2O_3-SiO_2$



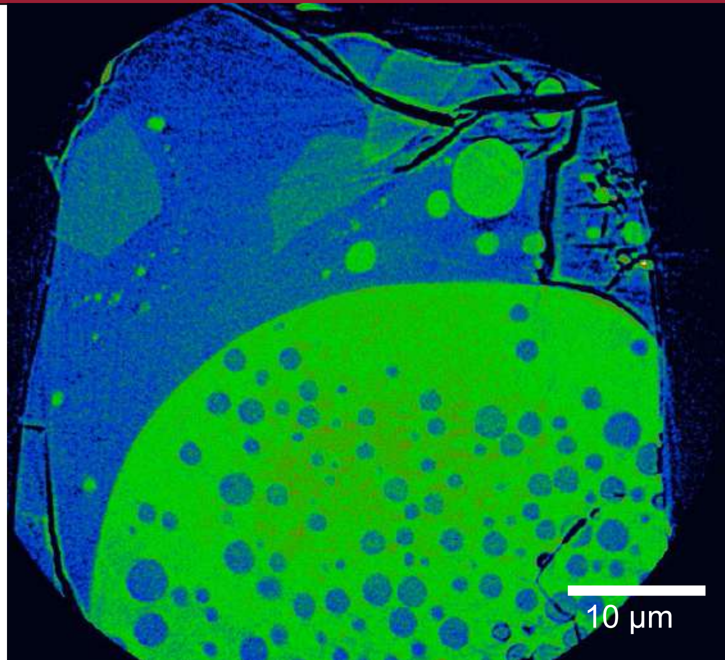
Mysen & Richet, *Silicate Glasses & Melts,* Fig 6.1, 2005

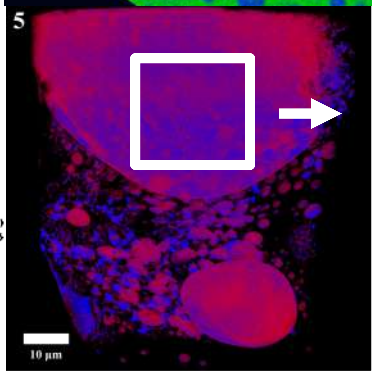


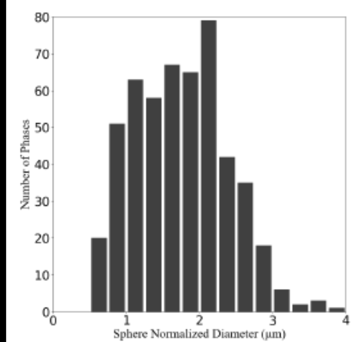
Levin & Cleek, JACERS 41, 175 (1958)



Goal: quench 2 immiscible glass phases

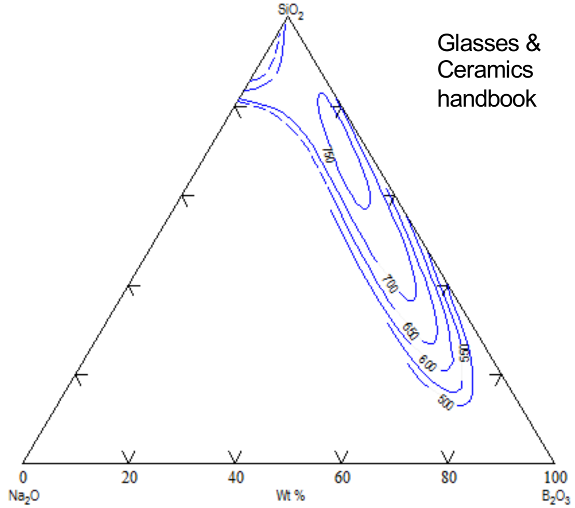






Bussey et al, *JNCS* 600, 121987 (2023)

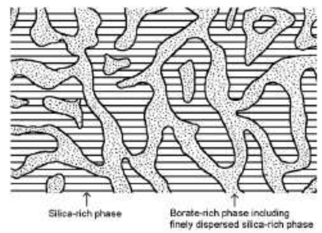
$Na_2O-B_2O_3-SiO_2$



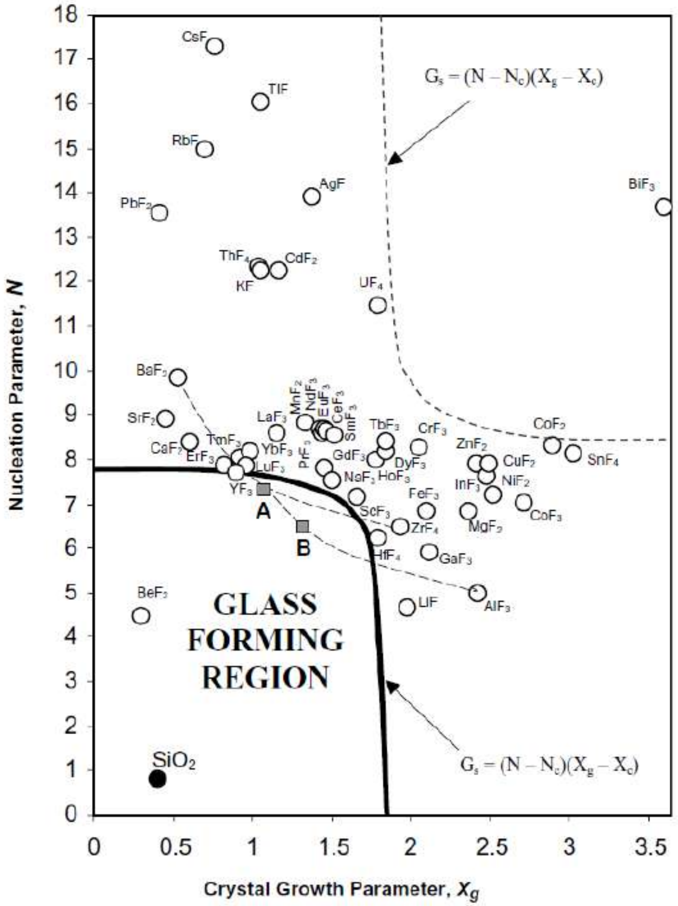
Glasses & Ceramics handbook

Leachable alkali borosilicate (Vycor, spinodal) – wt%

SiO_2	B_2O_3	Na_2O
65	26	9

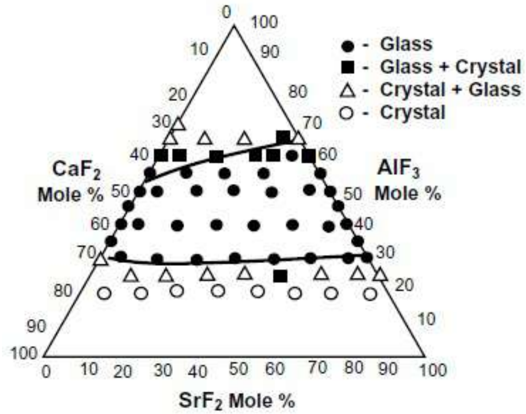


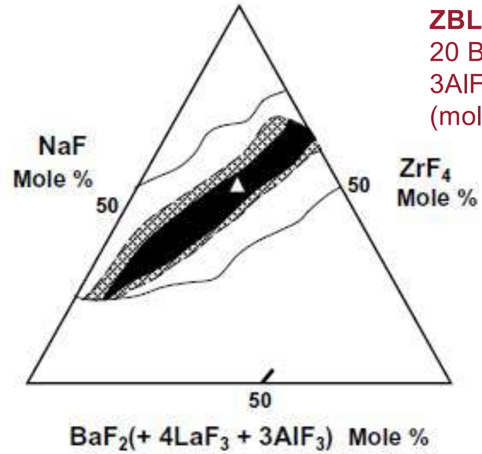
Parameterization: Designing fluoride systems



- Estimations of nucleation and growth effects in ionic glasses can be parameterized
  - Based on relations of viscosity at and below melting
- Parameters
  - Interatomic bond energy per volume
  - Ion volume
  - Entropy of fusion
- Tabulated data can be used to calculate glass stability (G_s) and estimate phase diagram boundaries for glass-forming
  - Good reproduction of experiments
  - Accurate prediction of ZBLAN stability

Experimental/theoretical glass forming regions



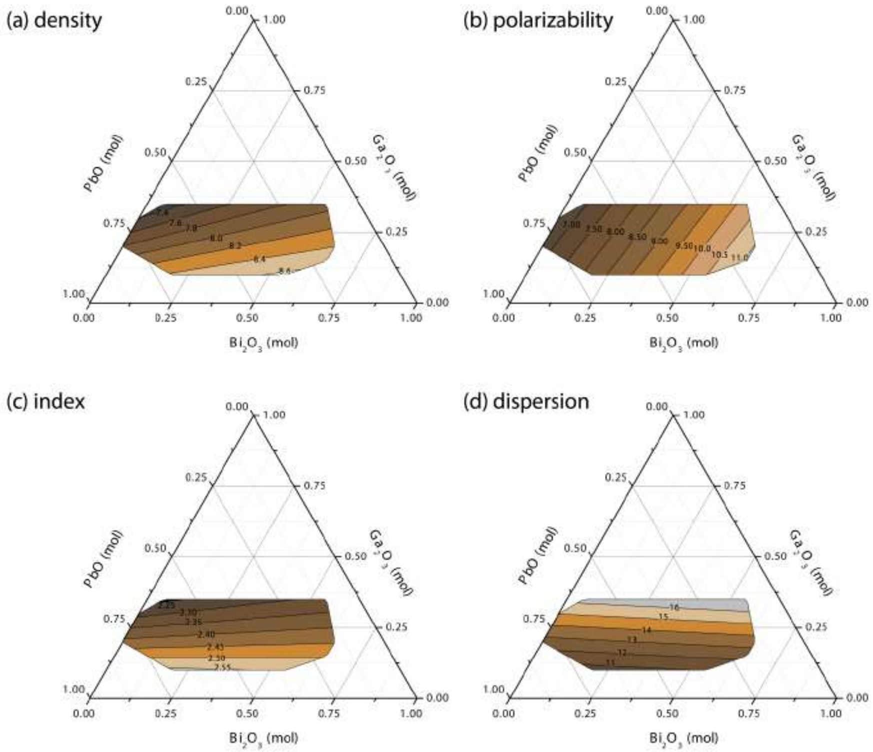


ZBLAN: 53 ZrF_4-20 BaF_2-4 LaF_3-3AlF_3-20 NaF (mole %)

Structural or chemical proxies: Optical basicity

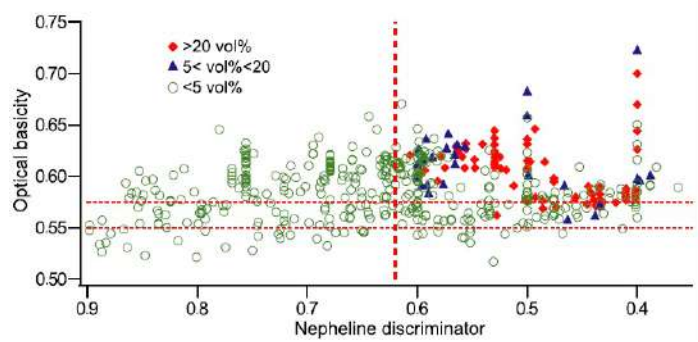
- Optical basicity
  - Polarizability of cations & oxygens
  - “Electron donating power”
- Applications
  - Optical properties
  - Redox states
  - Slag capacities
  - Crystallization

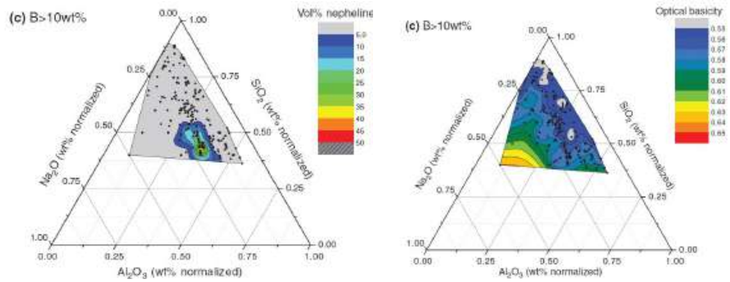
PbO-Bi_2O_3-Ga_2O_3



McCloy, Proc. SPIE 8016, 80160G (2011)

Nepheline crystallization in aluminosilicates





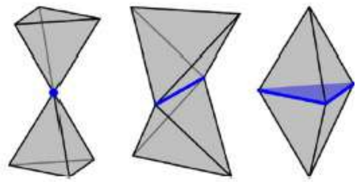
McCloy et al, *IJAGS* 2, 201 (2011)

Structural or chemical proxies:
Topological constraint theory

- Constraints and degrees of freedom
  - Stressed rigid vs floppy
  - More sophisticated topologies
- Affect many properties
  - Viscosity
  - Optical
  - Mechanical
  - Corrosion
  - Etc.
- Amenable to parameterization
- Other similar chemo-structural, e.g. polymerization (NBO/T)

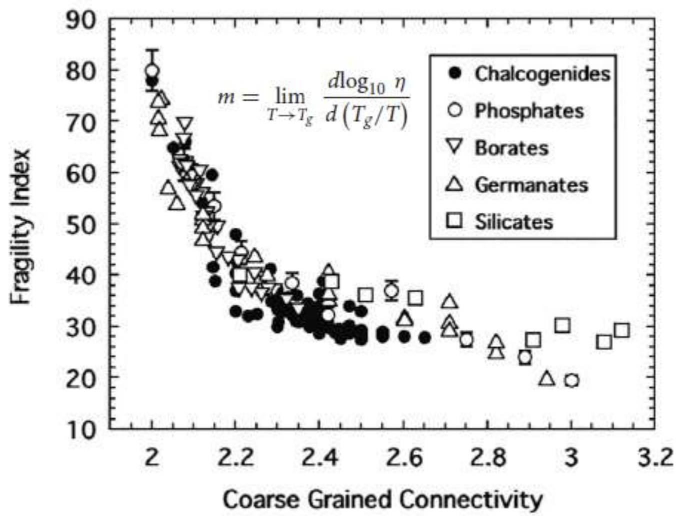
Phillips & Thorpe, *Solid St. Comm.* 53, 699 (1985)

Floppy, rigid, stressed-rigid



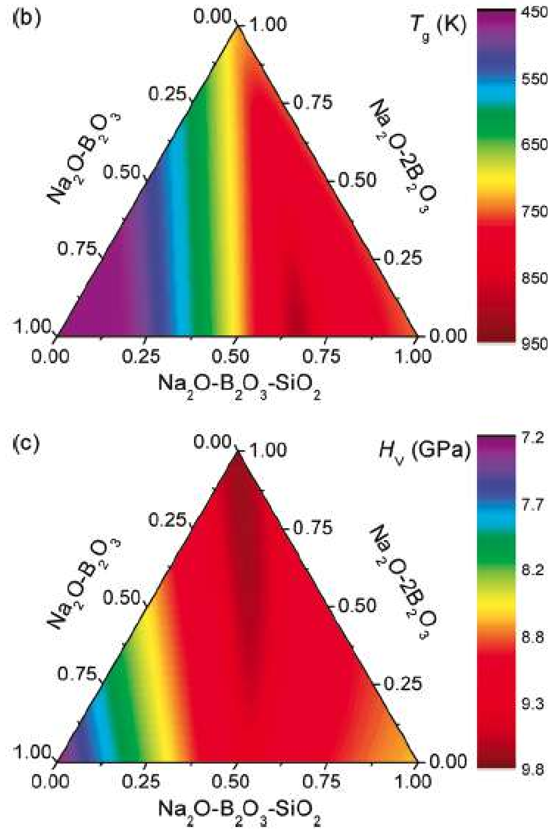
Sen & Mason, *Front. Mat*, 6, (2019)

Intersection of 0, 1, 2 polytopes



Sidebottom, *JNCS*, 534, 119641 (2019); *Front. Mat*, 6, 119641 (2019)

Temperature-dependent constraints



Smedskjaer et al, *JPCB*, 115, 12930 (2011)

Micolaut, Bauchy, Boolchand, Mauro, Sidebottom, etc.

Constraint theory: Designing chalcogenide systems

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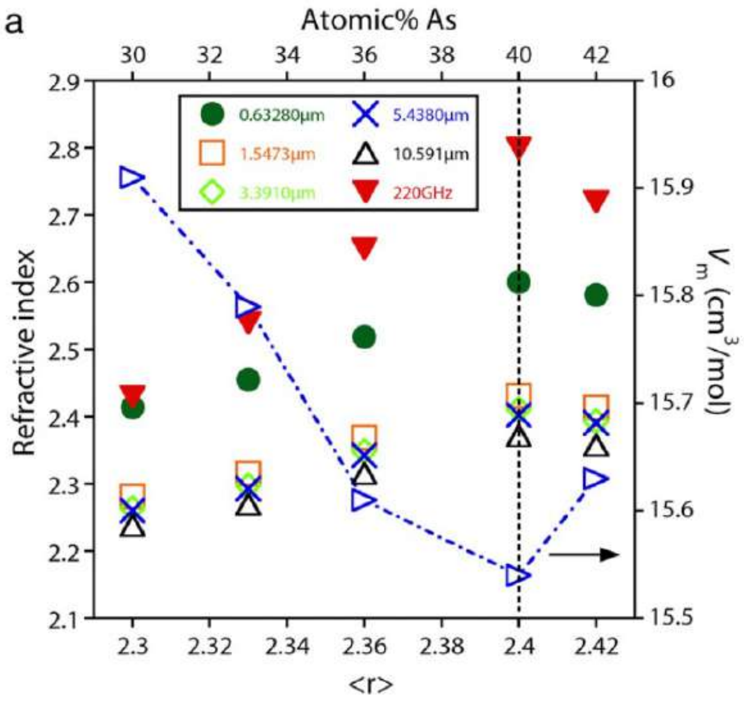
As-S



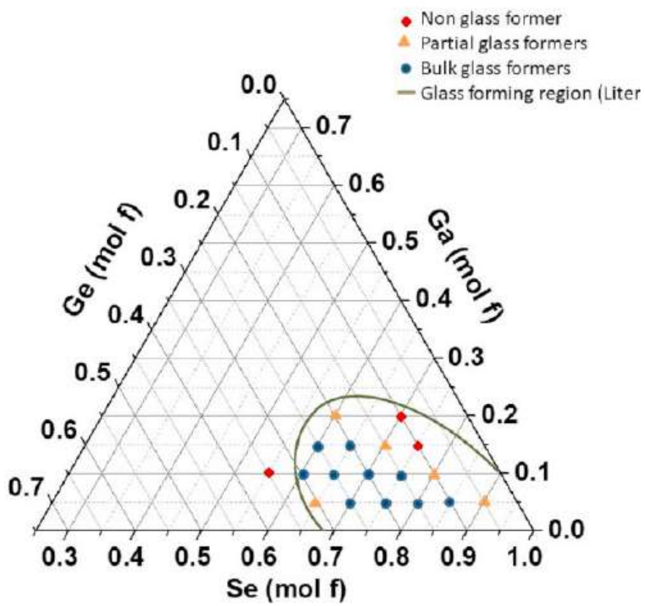
$$<r> = \sum_{n=1}^{i} x_i N_i = 3x_{As} + 2x_S.$$

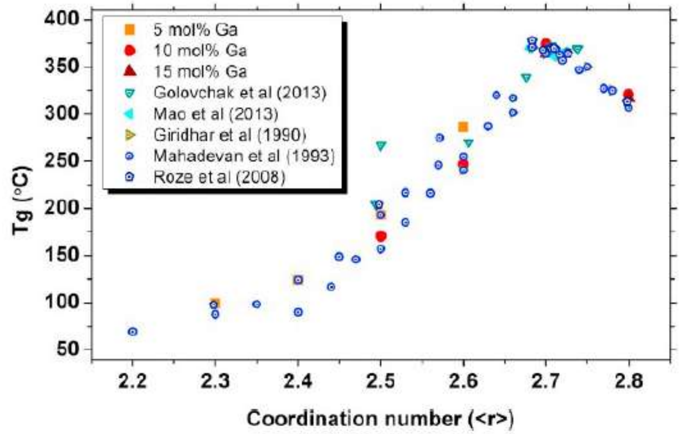
McCloy et al, *JNCS* 356, 1288 (2010)

Ge-Ga-Se

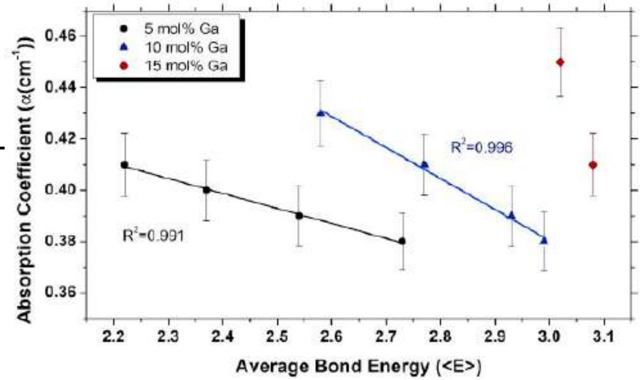
<r>: avg coordination #
(topological constraint theory)

<E>: mean atomic bond energy





λ=4.5 µm



Lonergan et al, *JNCS* 510, 192 (2019); 511, 115 (2019)

Example:
Substitutions in optical glasses

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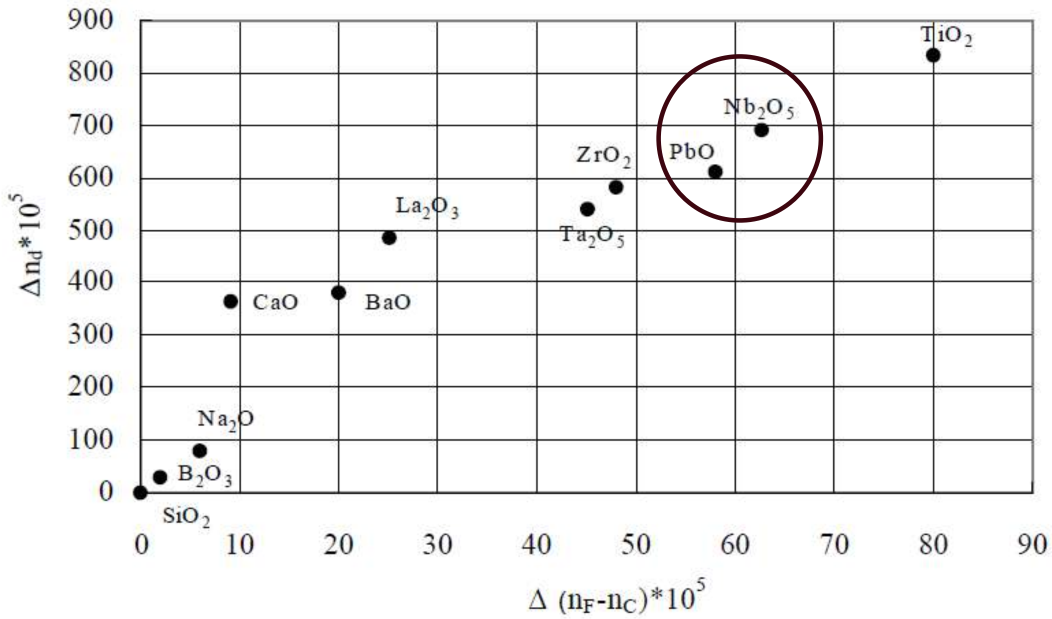
- "Environmentally friendly" – no As, Pb, Cd
- Have to figure out what component does
  - Decolorization, redox control (As)
  - Coloration (Cd)
  - Fining (As)
  - Polarizing power (Pb)
- One or more substitutions may be necessary
  - Murano glass (for As)
    - Substitutes (2012): CeO_2, blast furnace slag, but require higher temperature (1500 vs 1400˚C)
  - Ohara optical glass (for Pb)*
    - Nb_2O_5, TiO_2 in combination, low solubility



Substituting for Pb, need high index & dispersion

n_d = 587.6 nm; n_F = 486.1 nm; n_C = 656.3 nm

$PbO \rightarrow Nb_2O_5 + (TiO_2, ZrO_2)$

*Morishita & Onozawa, International Symposium Niobium 2001

Example: Substitutions in optical glasses

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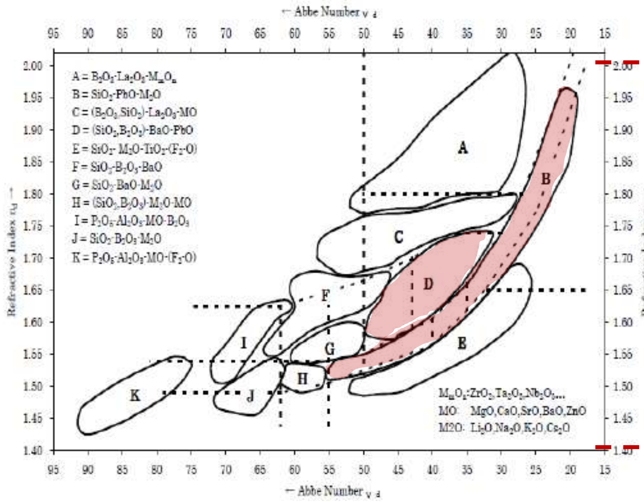
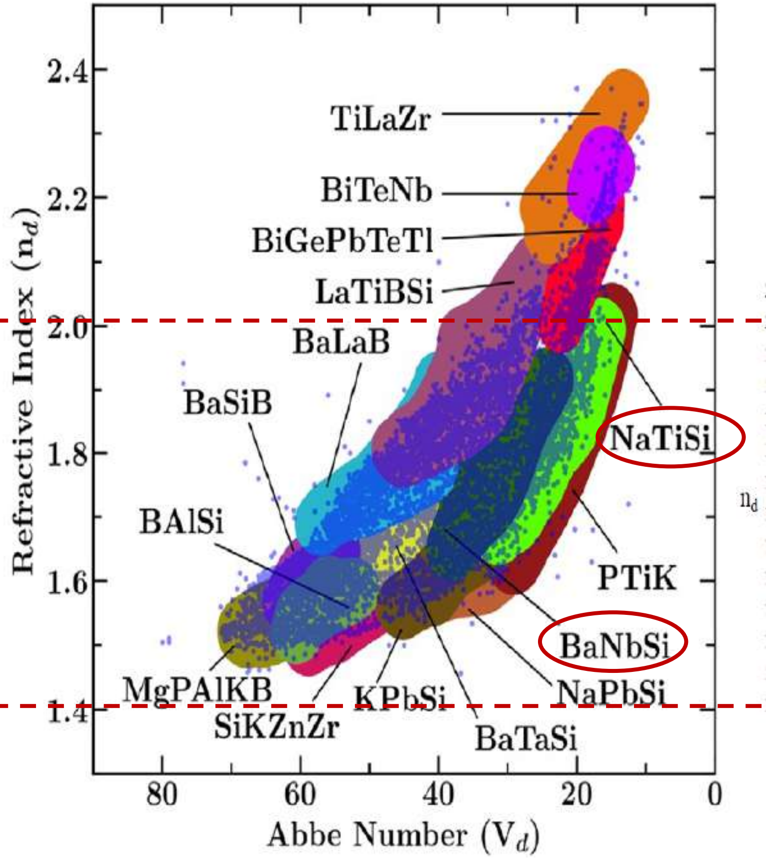
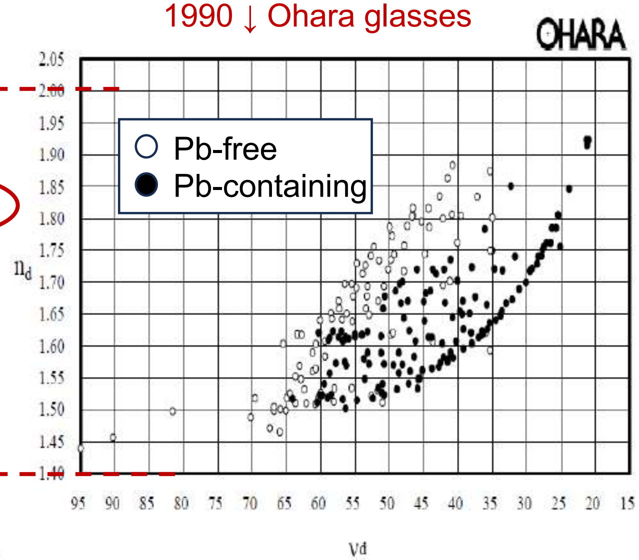
2001 ↓ General families
(Pb highlighted)





2022 Machine Learning (ML)
regions (w data)

1990 ↓ Ohara glasses



Morishita & Onozawa, International Symposium Niobium (2001)
Zaki…Krishnan, *JACERS,* 105, 4046 (2022)

Massive ML glass databases

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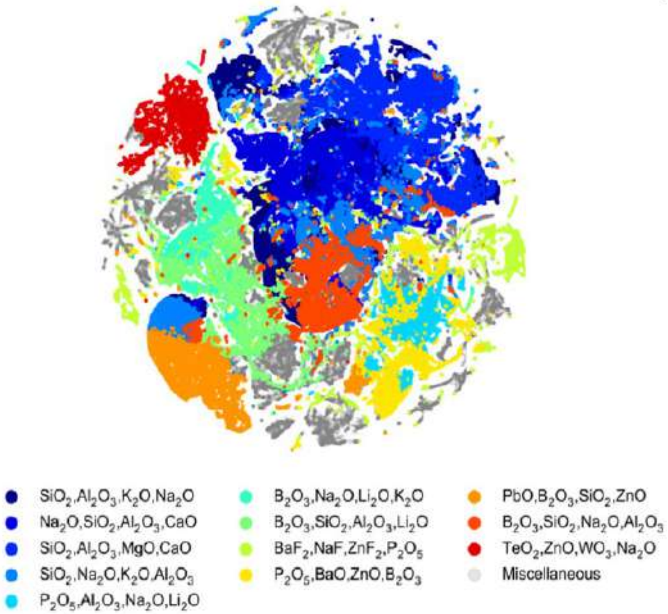
~275,000 compositions
221 different components (82 elements)
25 properties

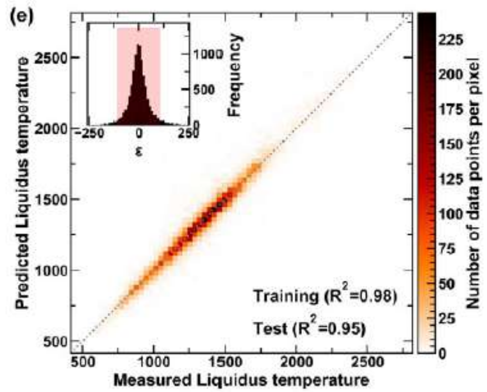


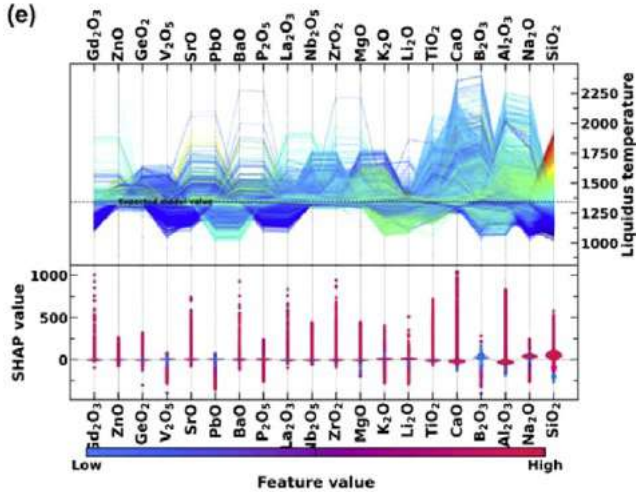
t-SNE to transform n-D to 2-D data

"Interpretable" machine learning algorithms:
Shapely Additive Explanations (SHAP) measuring interactions & importance

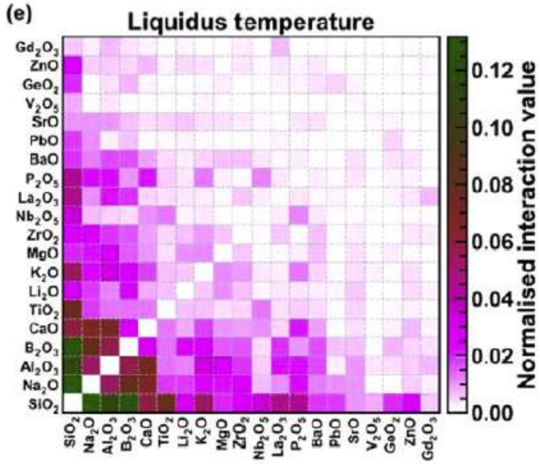
Properties modeled

- **Physical:** temperatures, thermal parameters
- **Mechanical:** moduli, hardness, density
- **Optical:** index, dispersion, transmittance
- **Electrical:** dielectric, conductivity





Ca, Sr, Al ↑T_L; Pb, B ↓T_L; alkali are **mixed**



Si strongly interacts with other formers (Al, B) and these all with modifiers (Na, Ca)

Bhattoo…. Krishnan, *Acta Materialia, 242,* 118439 (2023)

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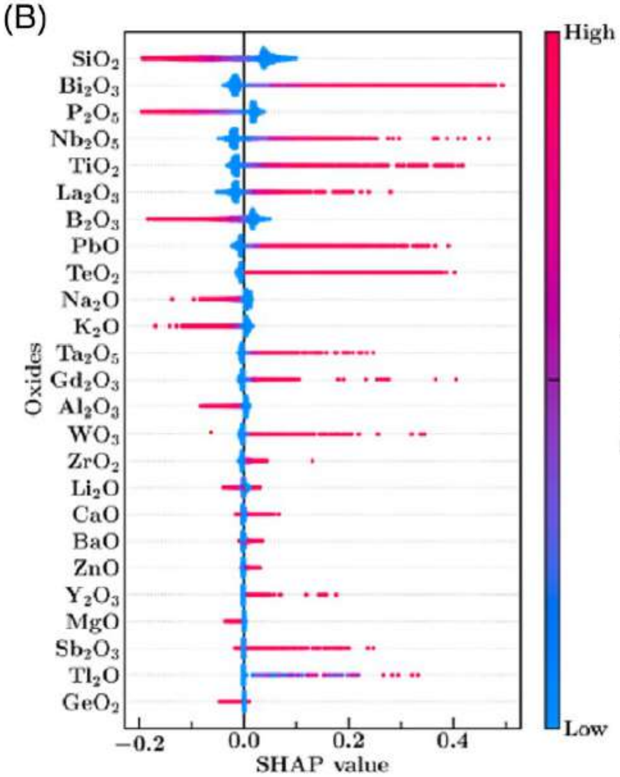
ML to help with optical glasses

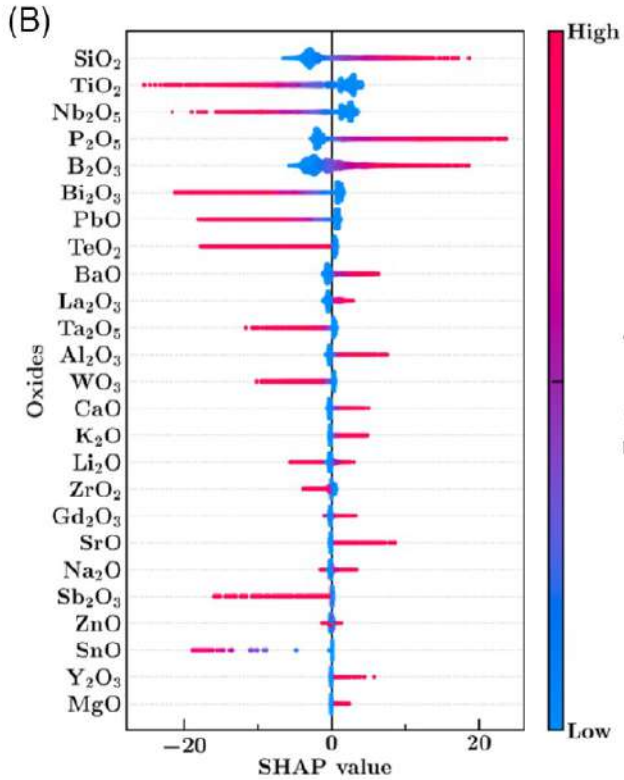
Refractive index: n_D



Red vs blue: Magnitude of the wt% of the oxide in considered compositions

- Negative effect
+ Positive effect

Dispersion (Abbe #): ν_D

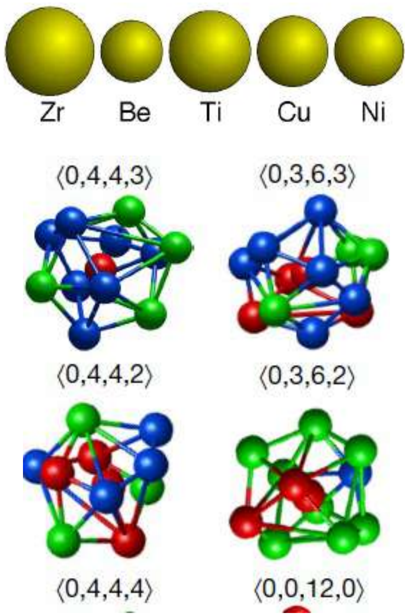


- SiO_2, P_2O_5, B_2O_3 (acidic oxides) ↓ index & ↓ dispersion (↑ ν_D)
- Bi_2O_3, Nb_2O_5, TiO_2, PbO, TeO_2, Sb_2O_3 ↑ index & ↑ dispersion (↓ ν_D)
- La_2O_3 identified as different: ↑ index & ↓ dispersion (↑ ν_D) weakly

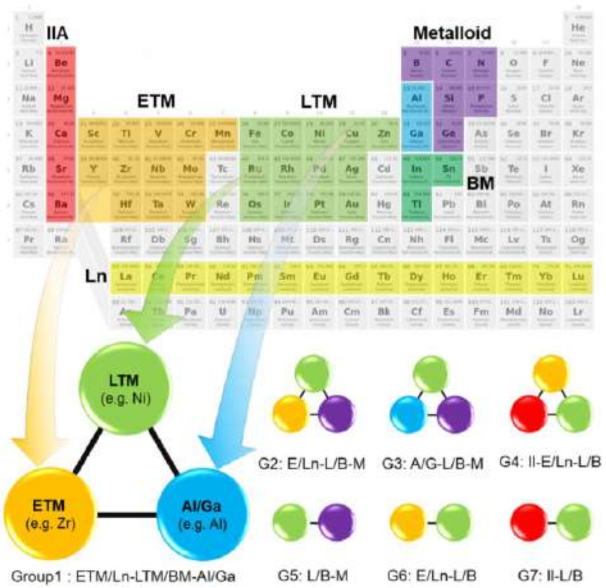
Zaki…Krishnan, *JACERS,* 105, 4046 (2022)

Metallic glasses

- Glass-forming ability (GFA) considered for metals
- Physics-informed grouping prior to ML better



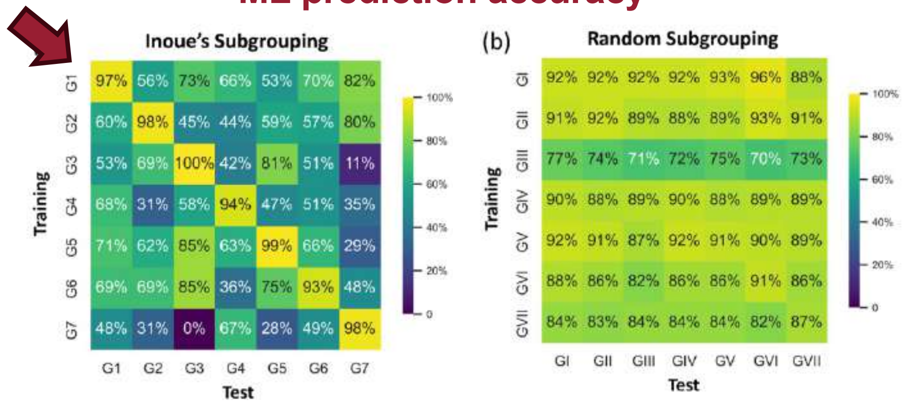
Relative size, packing



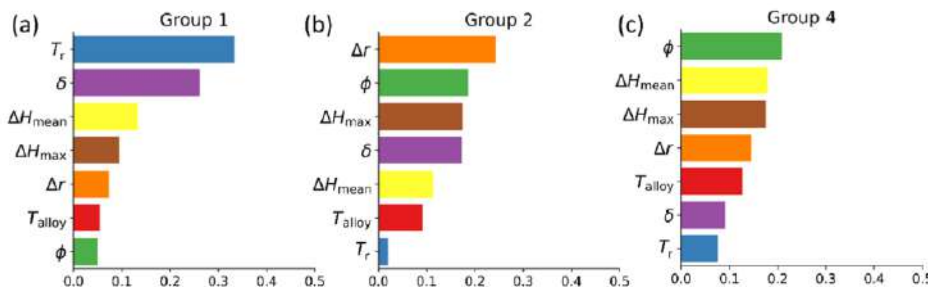
Inoue metallic glass (MG) groupings

1. ETM/Ln-LTM/BM-Al/Ga
2. ETM/Ln-LTM/BM-Metalloid
3. Al/Ga-LTM/BM-Metalloid
4. IIA-ETM/Ln-LTM/BM
5. LTM/BM-Metalloid
6. ETM/Ln-LTM/BM
7. IIA-LTM/BM

ML prediction accuracy



Importance for GFA differs between groups

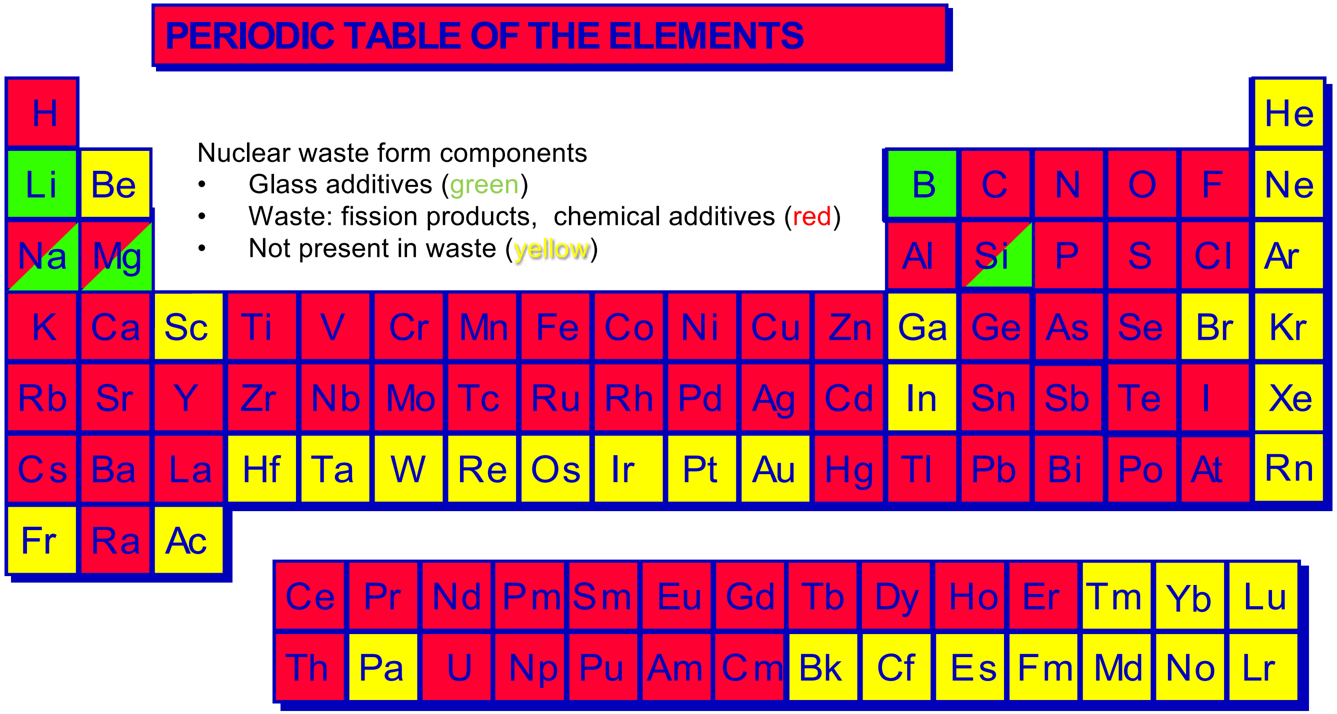


Factors

- $T_{liquidus\_alloy}$
- Atomic size difference/ ratio/ range
- Heat of mixing

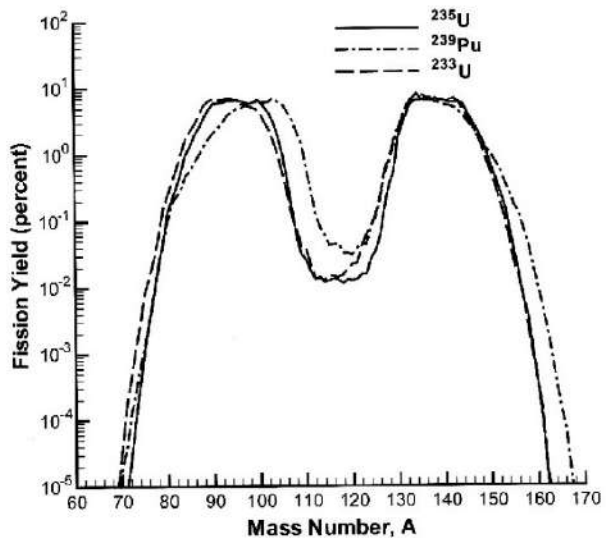
Liu et al, *Acta Materialia* 265, 119590 (2024)
Yang et al, *Nature* 592, 60 (2021)

Nuclear waste glasses: Context of the problem



Example, US defense waste

- Process chemicals
- Corrosion products
- Cladding
- **Fission Products**



Presence of large # of components makes traditional formulation methods difficult

Nuclear glasses: Composition-Property Modeling

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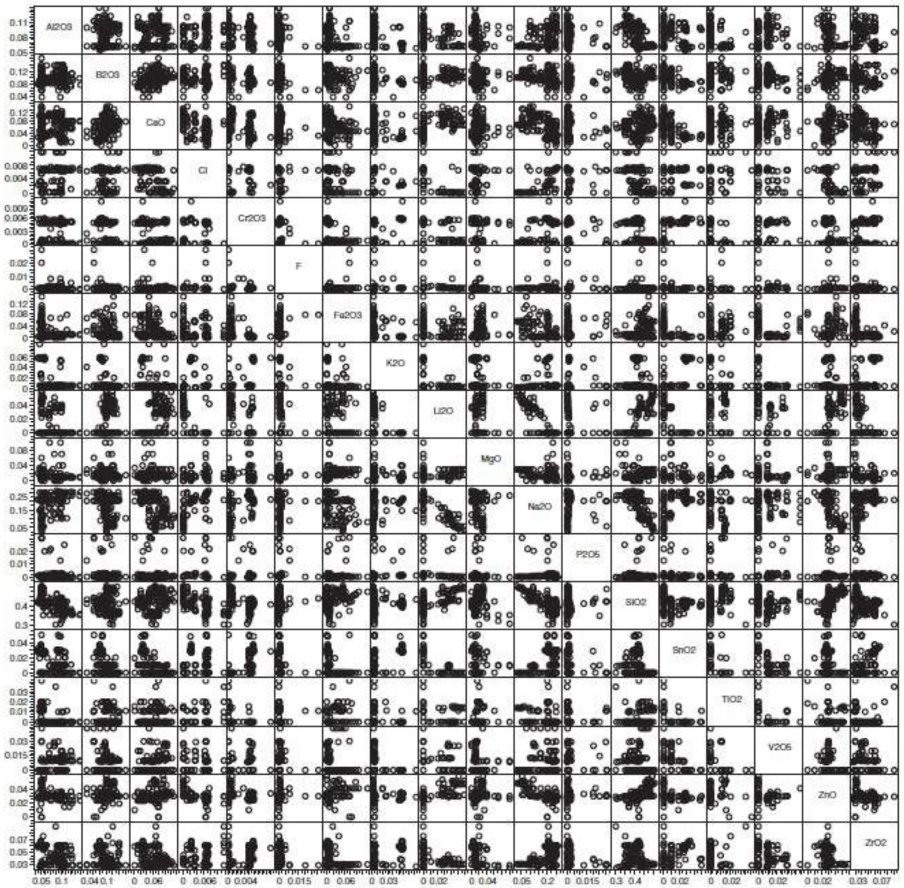
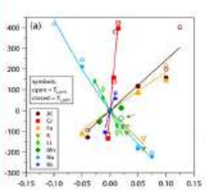
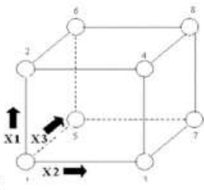
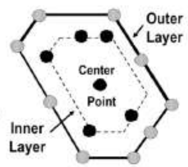
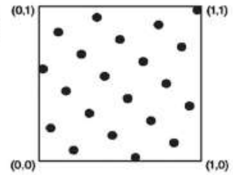
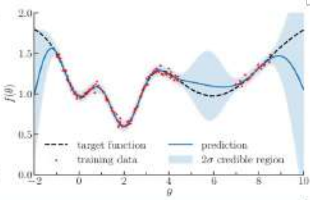


Fig. 1. Scatterplot matrix of component concentrations (normalized mass fractions) in the modeling dataset.

"Matrix glasses": Vienna, *JACERS* 2014

Increasing optimality →

Design Type	OCAT	Factorial	Extreme vertices	Space-filling	Autonomous (GPR based)
Graphic					
Pros	• Simple construction • Easy to visualize non-linear component effects	• Simple construction • Estimates cross-term effects	• Few points per variable • Some non-linear effects	• Non-linear effects (single components and cross term) • Few extreme compositions	• Non-parametric • Find compositional spaces with large uncertainty
Cons	• No cross-term effects • Many points per variable	• Many points per variable • Linear effects only • Extreme compositions	• Challenging to construct extreme compositions	• Challenging to construct	• High computational costs

Lu, X, et al. 2023. *J. Am. Ceram. Soc.* DOI:10.1111/jace.19333

Methods:

- Statistical approaches
- Neural networks
- Data science
- Machine-learning

Model composition effects for:

- Corrosion tests
- Crystallization
- Structure

Quantitative Structure Property Relations (QSPR)

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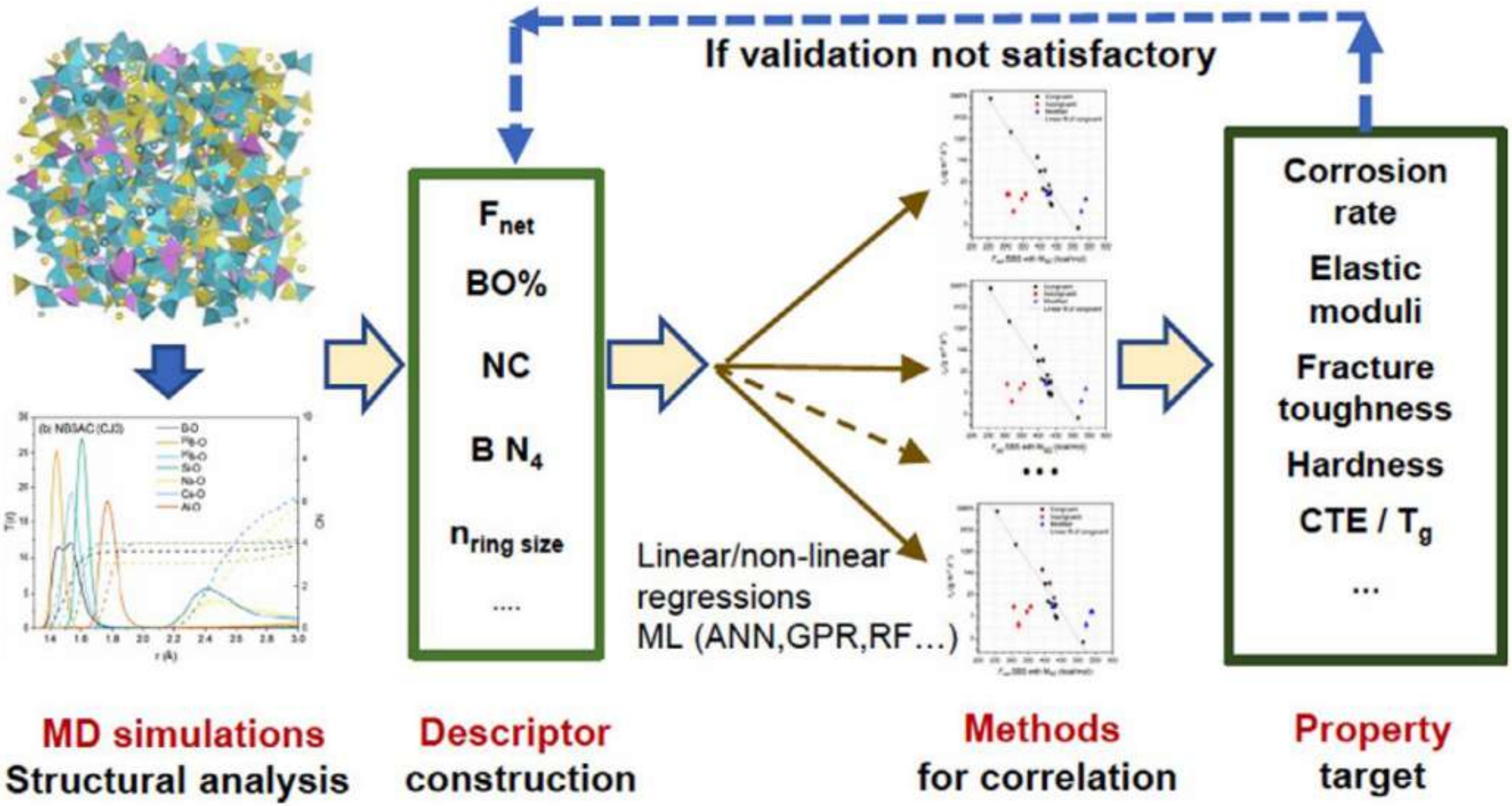

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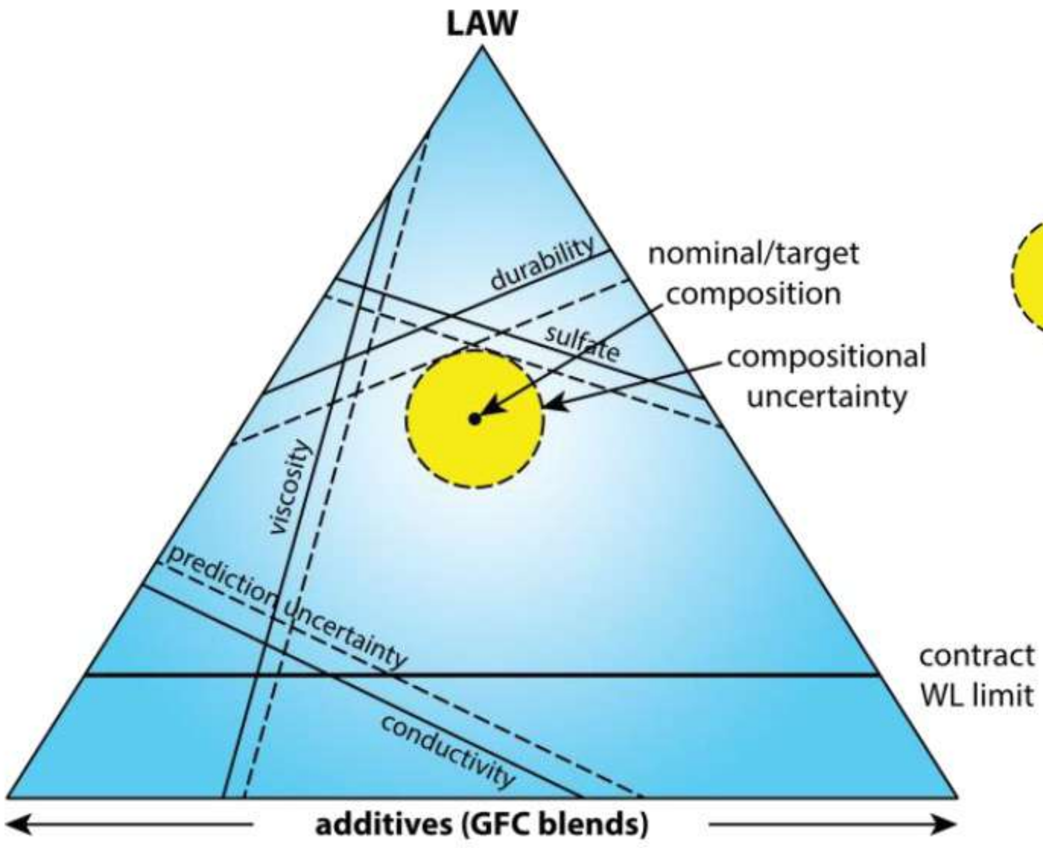
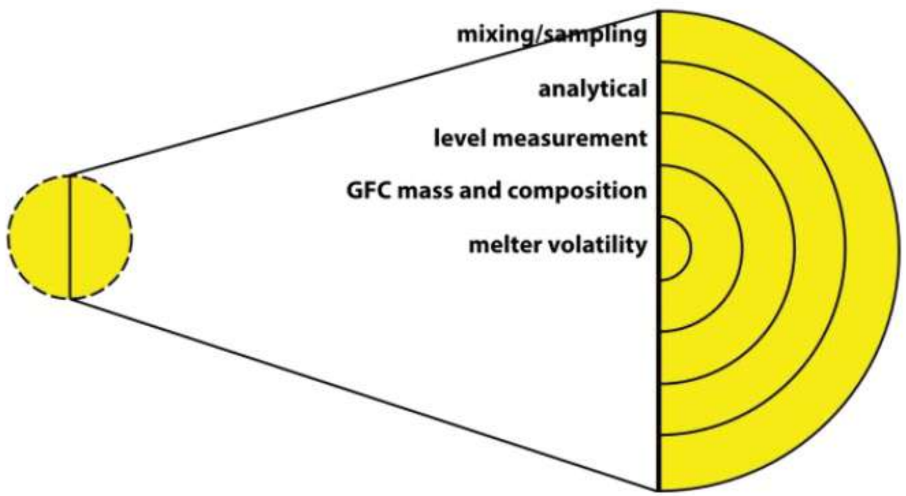
RUTGERS THE STATE UNIVERSITY OF NEW JERSEY

Du…Vienna, *JACERS*, 104,4445 (2021)
Zhang…Goel, *Acta Materialia, 268,* 119784 (2024)

Nuclear glasses: Formulation and Uncertainty





Optimization for highest waste loading considering **constraints & uncertainties**

Glass-ceramics

Processes for Glass-Ceramic Fabrication

growth (G)

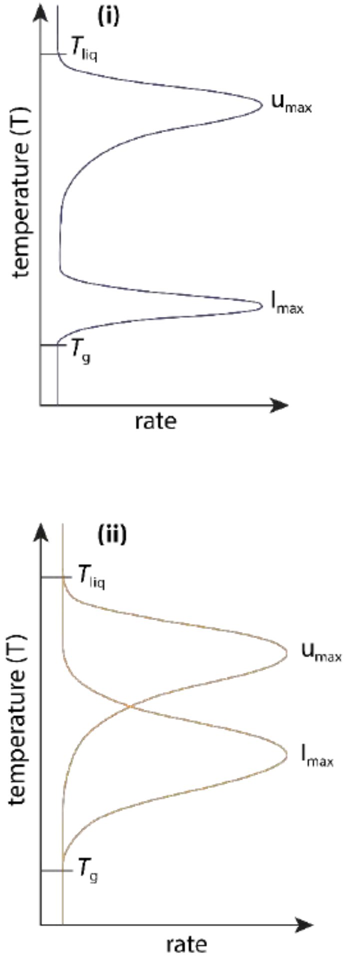
Separated

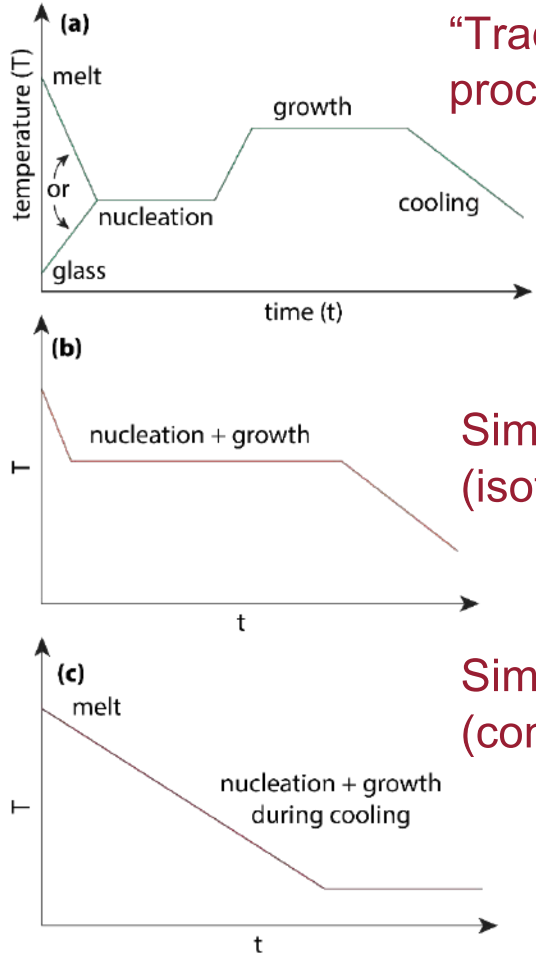
nucleation (N)

growth

Overlapping

nucleation





"Traditional" GC processing

Simultaneous N&G (isothermal)

Simultaneous N&G (continuous cool)

McCloy & Goel, *MRS Bulletin*, 42, 233 (2017)

Nuclear waste GC: Design issues

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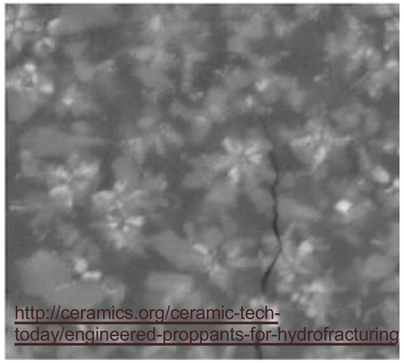
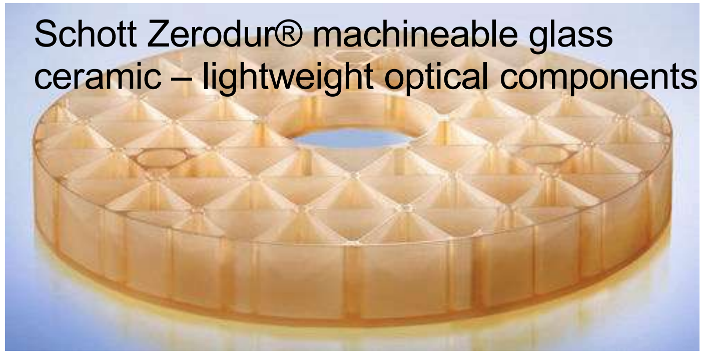
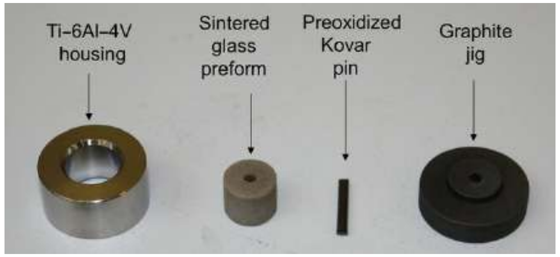
- **Consider waste composition (elements) & form (solid, liquid)**
  - Identify problematic components for solubility (e.g., Pu) and durability (e.g., Na)
- **Identify desired crystalline phases**
  - Add components to produce these phases (e.g. TiO_2)
  - Consider substitutional flexibility of target crystals (for waste ions)
  - Design for tolerance of waste variability
- **Design suitable melt chemistry**
  - Add components to create glass (e.g. SiO_2, B_2O_3)
  - Consider undissolved phases, source chemicals, intermediate reactions, volatility
  - Consider any amorphous phase separation
- **Design appropriate thermal profile**
- **Ensure processability**
  - Low enough liquidus temperature; high enough electrical conductivity
- **Ensure product stability**
  - Radiation hardening (e.g. amorphizing phases)
  - Chemical durability (e.g. glass/crystalline interfaces, residual glass)

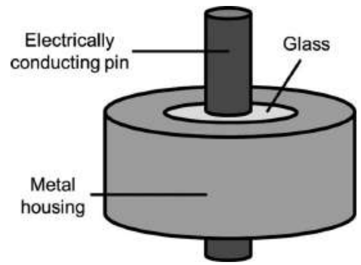
Other GC considerations

- Applications:
  - Radomes
  - Cookware
  - Telescopes
  - Seals
- Properties
  - Optical:
    - Crystallite size, relative index, transparency
  - Thermal:
    - Shock, CTE mismatch
  - Mechanical
    - Toughness
  - Electrical/ dielectric









Staff et al, *Int J Appl Ceram Tech* 13, 956 (2016)

http://www.cmog.org/article/discovery-waiting-happen-glass

Molla et al, *JACERS* 100, 1963 (2017)

Nuclear waste GC: Phase formed below liquidus T

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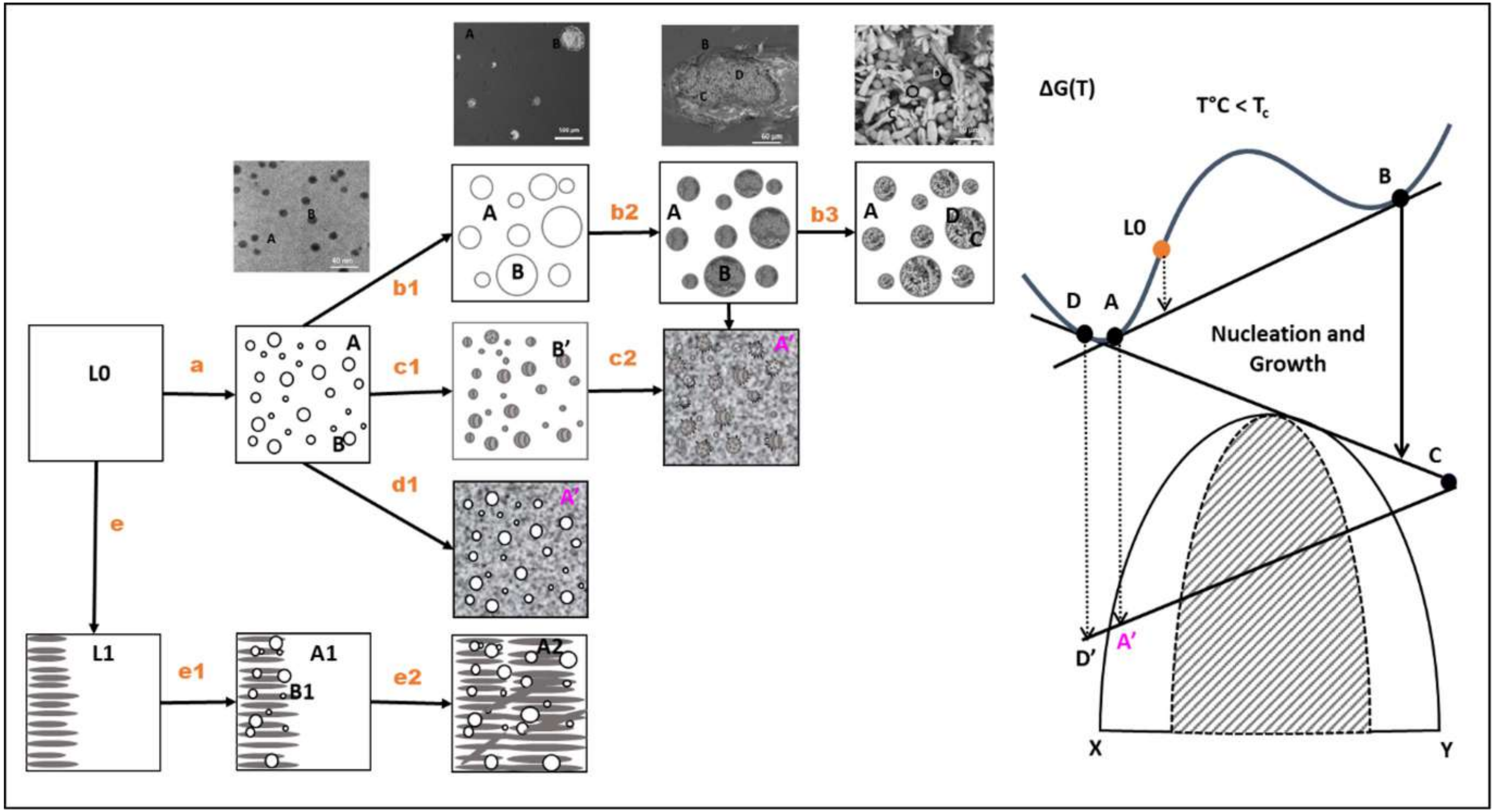
During glass synthesis or during cooling, **microscopic or macroscopic phase separation and crystallization** can occur **in the melt or in the glass**

Am, Nd, La, Pr (M^{3+})	→	Rare earth and actinide silicates: $Ca_2(Ln,An)_8(SiO_4)_6O_2$
Fe, Ni, Cr (M^{2+}, M^{3+})	→	Spinel : AB_2O_4
Pu, U, Ce, Zr (M^{4+})	→	$(Ce,Zr)O_2$, Pu, U, oxides
$Tc^{4+/7+}$, $Re^{4+/7+}$	→	Alkaline pertechnetate, perrhenate
Noble metals (Ru, Pd, Rh) M^0,M^{4+}	→	RuO_2, $(Ru,Rh)O_2$, PdTe, (Pd,Rh)Te
Mo (M^{6+})	→	**Phase separation and crystallization** of alkali & AE molybdates Na_2MoO_4, $CsNaMoO_4$, Li_2MoO_4, Na_2MoO_4, $CaMoO_4$, $MgMoO_4$, $CsNaMoO_4$, $Cs_3Na(MoO_4)_2$ $CsLiMoO_4$ $Na_3Li(MoO_4)_2$,$CaMoO_4$
Si^{4+}, Al^{3+}	→	Quartz, nepheline, eucryptite, Li silicate

Ln = lanthanides
An = actinides

Schuller, 2022

Mechanisms of phase separation & crystallization



McCloy and Schuller, *Comptes Rendus. Géoscience,* 354(S1), 121 (2022)

Phase separation & crystallization → Microstructure

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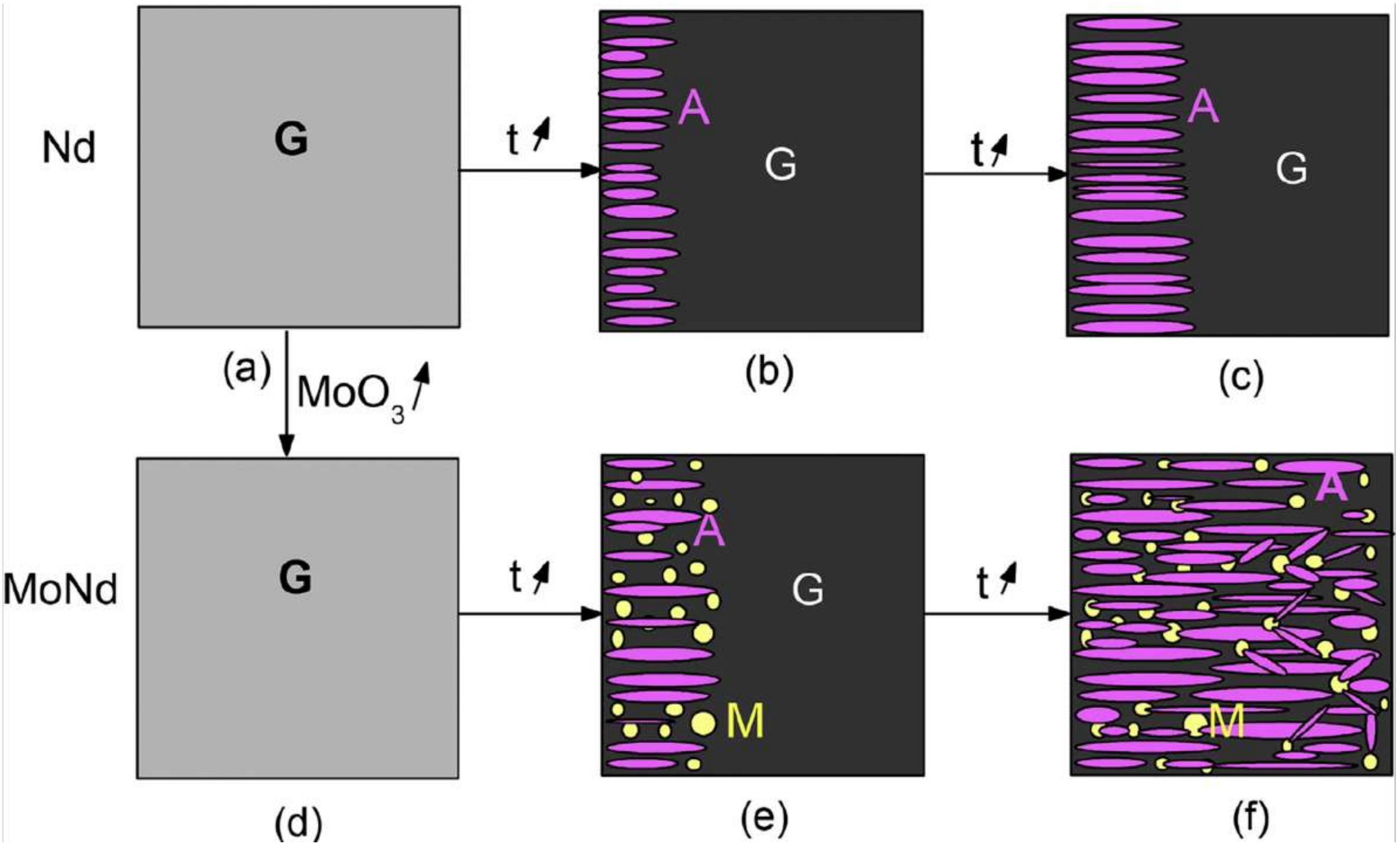

Glass

Apatite
$Ca_2Nd_8(SiO_4)_6O_2$

Molybdate, e.g. powellite $CaMoO_4$

Chouard et al, *Journal of Alloys and Compounds*, 671, 84 (2016)

Leave-one-out formulation example

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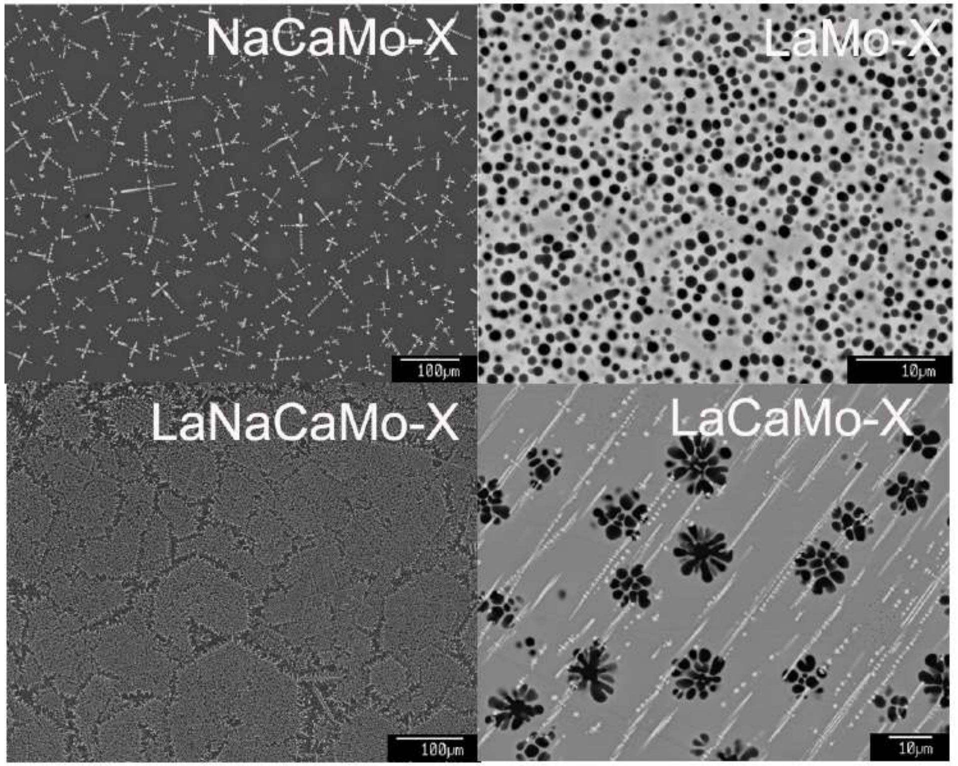
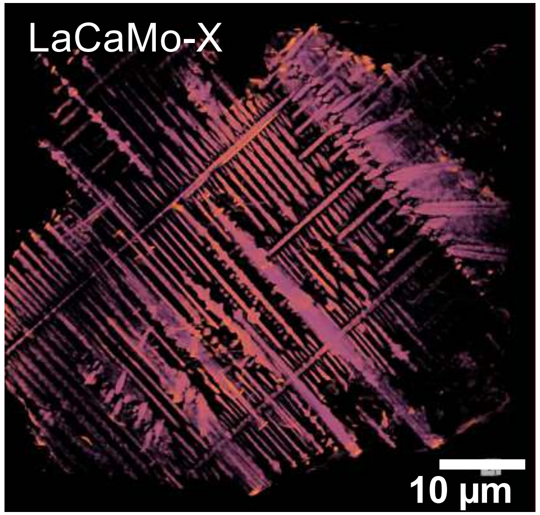
Leave out: RE_2O_3, Na_2O, or MoO_3
Leave out both: Na_2O, CaO
Change RE: La, Ce, Nd, Sm, Er, Yb

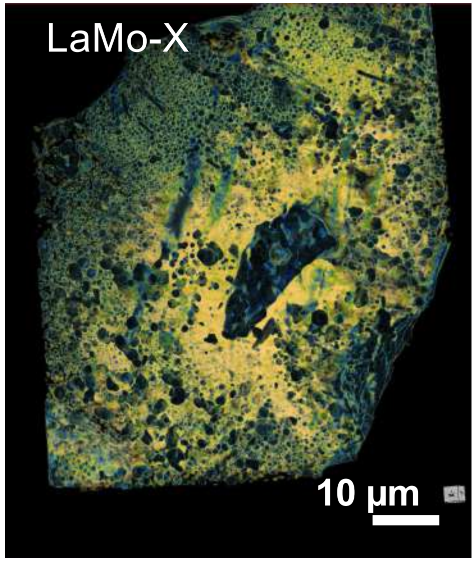


Patil et al, *J. Nucl. Mater.*, 510, 539 (2018)

Chemical compositions of the target samples in mol%.

Sample Name	RE_2O_3	Na_2O	CaO	MoO_3	SiO_2	B_2O_3	Al_2O_3	ZrO_2
NaCaMo	–	12.14	13.58	3.53	50.51	11.95	5.14	3.15
LaNaCaMo	4.93	11.54	12.91	3.36	48.02	11.36	4.89	2.99
LaCaMo	4.93	–	24.45	3.36	48.02	11.36	4.89	2.99
LaMo	6.53	–	–	4.45	63.56	15.04	6.47	3.96
LaNaCa	5.10	11.94	13.36	–	49.69	11.75	5.06	3.10



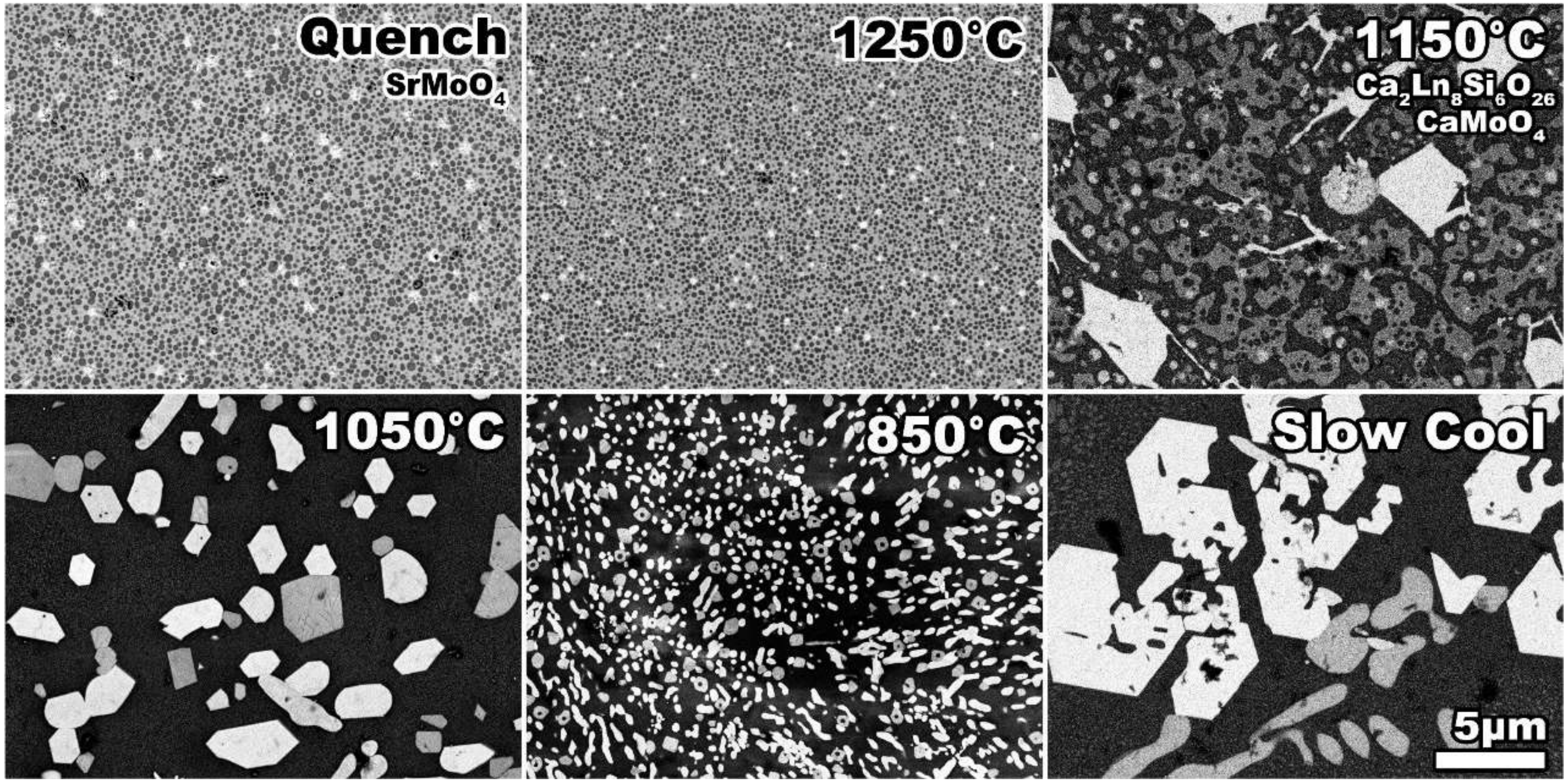


Nano-CT

Bussey et al, *JNCS*, 600, 121987 (2023)

Heat treatment examples

Same composition, different heat treatments



Courtesy Jarrod Crum, PNNL

Conclusions

- Numerous methods and strategies exist for glass formulation depending on the goals and level of complexity
    - Simple empirical substitutions -> phase diagrams -> physics based -> complex ML analyses
    - All families of glass: oxide, chalcogenide, fluoride, metallic
- Process-properties-product-composition should be considered
    - Raw material substitutions
    - Process-induced impurities
    - Performance envelopes
- Glass-ceramics have additional formulation considerations
    - Glass vs crystal phase partitioning
    - Heat treatment and microstructure development

Acknowledgements

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And YOU for your attention!

Gracias por escuchar!
Gràcies per la seva atenció